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Effects of edges in spin-$\frac{1}{2}$ bond-alternating Heisenberg chains: Matrix-product variational approach

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We make a matrix-product variational approach to spin-$\frac{1}{2}$ ferromagnetic-antiferromagnetic bond-alternating chains with anisotropy on their ferromagnetic bonds, especially under the open boundary condition. The rich phase diagram containing the Haldane, large-D, and two types of Néel phases is well reproduced with only two variational parameters. The on-bond anisotropy has a significant effect on the ferromagnetic coupling between neighboring spins and induces novel edge states peculiar to spin-$\frac{1}{2}$ chains.

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Haldane's conjecture [1, 2] sparked renewed interest in low-dimensional quantum magnets and led to extensive explorations of spin gaps—energy gaps in magnetic excitation spectra. While the early research centered on spin-1 antiferromagnetic chains, spin-$\frac{1}{2}$ bond-alternating chains have been attracting further interest due to their enriched ground-state properties [3, 4, 5, 6, 7, 8]. A spin-$\frac{1}{2}$ Heisenberg chain with alternating ferromagnetic and antiferromagnetic couplings converges to the spin-1 antiferromagnetic Heisenberg chain as the ferromagnetic coupling tends to infinity, where the ground state remains unique and gapful for all the ratios of the two exchange couplings [3]. Thus the spin-1 Haldane gap turns out to be continuously connected to the gap originating in decoupled singlet dimers. Such a consideration can be verified for existent bond-alternating chain compounds such as IPACuCl$_3$ (IPA = isopropylammonium = $(CH_3)_2CHNH_3$) [9] and (4-BzpipdH)CuCl$_3$ (4-BzpipdH = 4-benzylpiperidinium = $C_{12}H_{18}N$) [10]. These materials indeed reproduce many of observations common to Haldane-gap antiferromagnets [11, 12, 13, 14]. With increasing temperature, the effective spin-1 features disappear into the spin-$\frac{1}{2}$ paramagnetic behavior [15, 16, 17].

Apart from paramagnetic spin $\frac{1}{2}$'s, quantum spin-$\frac{1}{2}$ degrees of freedom lie in spin-1 Haldane-gap antiferromagnets [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28]. In more general, there appear fractional spin-$\frac{S}{2}$ degrees of freedom on boundaries of antiferromagnetic Heisenberg chains with integral spin S at low temperatures [29, 30]. The chain-end fractional spins are understandable in view of the valence-bond-solid states [31, 32] and were actually observed for both spin-1 [33, 34, 35] and spin-2 [36] antiferromagnetic chain compounds. Such observations are peculiar to the Haldane phase. Hence both quantum and classical spin-$\frac{1}{2}$ degrees of freedom may be observed for Haldane-gap materials composed of spin $\frac{1}{2}$'s. Thus motivated, we study spin-$\frac{1}{2}$ ferromagnetic-antiferromagnetic bond-alternating chains with particular emphasis on their edge states, making good use of the matrix-product representation as well as a quantum Monte Carlo method.

The Hamiltonian of our interest is given by

$$\mathcal{H}=\sum_{j=1}^{N}\big[-J_{\rm F}\boldsymbol{S}_{2j-1}\cdot\boldsymbol{S}_{2j}+J_{\rm AF}\boldsymbol{S}_{2j}\cdot\boldsymbol{S}_{2j+1} +D(S^z_{2j-1}+S^z_{2j})^2\big], \tag{1}$$

where $J_{\rm F}$ and $J_{\rm AF}$ are both set positive. The on-bond anisotropy D, which is related to a single ion anisotropy in the case of spin 1, originates from possible dipole-dipole and/or anisotropic exchange interactions between the ferromagnetically coupled spin $\frac{1}{2}$'s [15]. When we consider a wave function of the matrix-product type:

$$|\Psi\rangle=\mathrm{Tr}[g_1\otimes g_2\otimes\cdots\otimes g_N], \tag{2}$$

employing the complete set of states on the jth ferromagnetic bond:

$$|s\rangle_j=\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_j-|\downarrow\uparrow\rangle_j),\quad |t_-\rangle_j=|\downarrow\downarrow\rangle_j,$$
$$|t_0\rangle_j=\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_j+|\downarrow\uparrow\rangle_j),\quad |t_+\rangle_j=|\uparrow\uparrow\rangle_j, \tag{3}$$

the decoupled dimers for $J_{\rm F}\to 0$ are described by

$$g_j=\begin{pmatrix}|s\rangle_j+|t_0\rangle_j & -\sqrt{2}|t_+\rangle_j\\ \sqrt{2}|t_-\rangle_j & |s\rangle_j-|t_0\rangle_j\end{pmatrix}, \tag{4}$$

while the optimum ground state for $J_{\rm F}\to\infty$ is given by

$$g_j=\begin{pmatrix}|t_0\rangle_j & -\sqrt{2}|t_+\rangle_j\\ \sqrt{2}|t_-\rangle_j & -|t_0\rangle_j\end{pmatrix}. \tag{5}$$

The g matrices (5), with their indices contracted, create singlet bonds in between [37] and end up as the spin-1 valence-bond-solid state [32]. The g matrices (4) can be used as the basis for a variational calculation [38] of the Hamiltonian (1) by allowing different amplitudes for the singlet and triplet contributions and reducing the rotational invariance as

$$g_j=\begin{pmatrix}b|s\rangle_j+c|t_0\rangle_j & -\sqrt{2}a|t_+\rangle_j\\ \sqrt{2}a|t_-\rangle_j & b|s\rangle_j-c|t_0\rangle_j\end{pmatrix}. \tag{6}$$

TABLE I: The matrix-product variational (MP) and quantum Monte Carlo (QMC) calculations of the ground-state energy per site for the isotropic ($D = 0$) chain.

$J_{\rm F}/J_{\rm AF}$	MP	QMC
0.2	−0.37678	−0.3768(1)
0.5	−0.38538	−0.3855(1)
1.0	−0.41197	−0.4125(1)
2.0	−0.49435	−0.4976(1)
5.0	−0.82583	−0.8426(1)

The isotropic chain is described by equalizing c to a and the two extreme cases (4) and (5) are indeed included in this ansatz. Then, eq. (2) gives a variational ground state of the periodic chain, while each of the four elements of the 2×2 matrix $g_1 \otimes g_2 \otimes \cdots \otimes g_N$ corresponds to a ground state of the open chain with fixed spins at each end. In the Haldane phase, the four states of the open chain are quasi-degenerate [39].

The variational energy $\langle\Psi|\mathcal{H}|\Psi\rangle/\langle\Psi|\Psi\rangle \equiv E_{\rm var}$ is calculated as

$$\frac{E_{\rm var}}{2N} = -J_{\rm F}\frac{2|a|^2-3|b|^2+|c|^2}{4(2|a|^2+|b|^2+|c|^2)} - J_{\rm AF}\frac{2|a|^2(|b|^2+|c|^2+3|b||c|)+|a|^4+|b|^2|c|^2}{(2|a|^2+|b|^2+|c|^2)^2} + D\frac{2|a|^2}{2|a|^2+|b|^2+|c|^2}, \tag{7}$$

and its bounds are compared with quantum Monte Carlo findings in Table I. The variational estimates are less precise in the region of strong ferromagnetic coupling but still agree with the numerical values within two-percent error even at $J_{\rm F}/J_{\rm AF} = 5.0$. The spin correlation function and local moments induced on a chain end are also calculated and verified in Fig. 1. Considering that the correlation length is considerably underestimated by

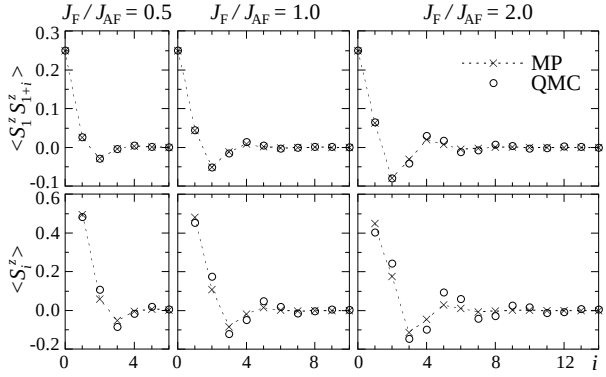

FIG. 1: The matrix-product variational (MP) and quantum Monte Carlo (QMC) calculations of the spin correlations (the upper three) and moments (the lower three) in z direction for the isotropic ($D = 0$) open chains with ferromagnetic couplings at each end.

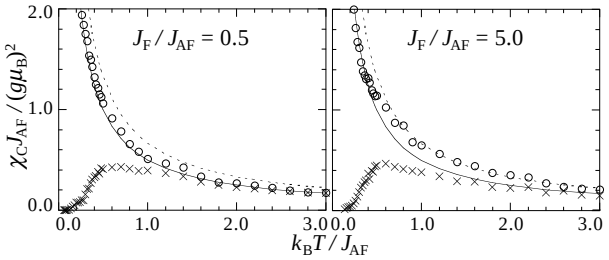

FIG. 2: Quantum Monte Carlo calculations of the Curie component in the magnetic susceptibility as a function of temperature for the isotropic ($D = 0$) open chains with ferromagnetic ($\circ$) or antiferromagnetic ($\times$) couplings at each end. The solid and dotted lines denote the Curie susceptibilities due to two spins of $S = \frac{1}{2}$ and a single spin of $S = 1$, respectively.

wave functions of the matrix-product type in general [40], our variational findings are fairly good. The variational expression for the z-component correlation length ξ,

$$\frac{1}{\xi} = \frac{1}{2}\ln\Big(\frac{|b|^2+|c|^2+2|a|^2}{|b|^2+|c|^2-2|a|^2}\Big), \tag{8}$$

is useful especially in the region of weak ferromagnetic coupling. The edge moments, which are assembled into an effective spin $\frac{1}{2}$, are characteristic of the Haldane phase [18, 20] and should therefore be observed for the present system with nonmagnetic impurities as well. Besides direct observations, we can detect them through magnetic susceptibility measurements [29, 30]. Figure 2 shows the Curie component of the susceptibility, $\chi^{\rm op.}_{2N+2} - \chi^{\rm per.}_{2N} \equiv \chi_{\rm C}$, where $\chi^{\rm per.}_L$ and $\chi^{\rm op.}_L$ are the susceptibilities of the periodic and open chains with L spins, respectively. Two excess moments of $S = \frac{1}{2}$ are found at both low and high temperatures. The low-temperature ones are quantum mechanically correlated effective spins induced at each end, whereas the high-temperature ones are paramagnetic spins of classical aspect. In the region of strong ferromagnetic coupling, such a difference can be understood better, because the distinct features of paramagnetic spin 1's appear at intermediate temperatures, where the Haldane phase is thermally broken but the ferromagnetic exchange interactions still survive. The open chain with antiferromagnetic couplings at each end exhibits no edge moment at low temperatures even in the Haldane phase.

Our variational scheme is still useful for the anistropic chain and well reproduces its rich phase diagram, as is shown in Fig. 3. With increasing $|D|$, the Haldane gap decreases to zero and there alternatively appear three distinct phases according to the sign of D and the ratio of $J_{\rm F}$ to $J_{\rm AF}$. The variational wave function illuminates in itself how the spin correlations vary with the anisotropy. Moving across the phase transitions, we plot in Fig. 4 the optimum variational parameters. Considering that eq. (6) is rewritten as

$$g_j = b|s\rangle_j\sigma^0 + a(|t^x\rangle_j\sigma^x + |t^y\rangle_j\sigma^y) + c|t^z\rangle_j\sigma^z, \tag{9}$$

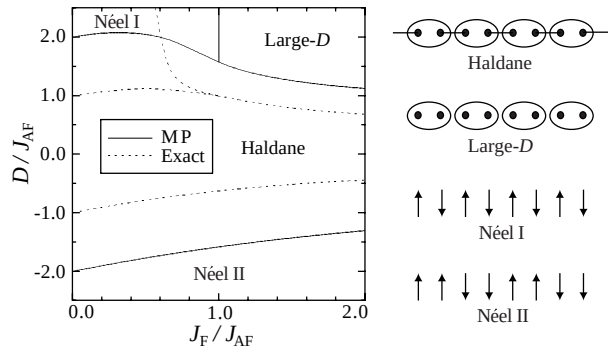

FIG. 3: The matrix-product variational (MP) and numerical diagonalization (Exact) [4] calculations of the ground-state phase diagram. Schematical representations of each phase are presented for reference, where the arrow (the bullet symbol) and the segment denote a spin $\frac{1}{2}$ with its fixed (unfixed) projection value and a singlet pair, respectively, while the circle means an operation of constructing a spin 1 by symmetrizing the two spin $\frac{1}{2}$'s inside.

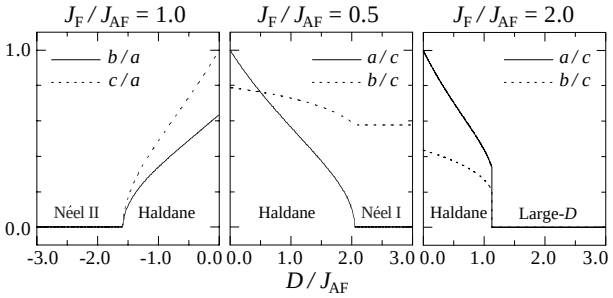

FIG. 4: The optimum variational parameters as functions of the ferromagnetic coupling and the on-bond anisotropy.

where $(|t^x\rangle_j \pm {\rm i}|t^y\rangle_j)/\sqrt{2} = |t_\pm\rangle_j$, $|t^z\rangle_j = |t_0\rangle_j$, and σ^0 and $(\sigma^x, \sigma^y, \sigma^z)$ are the 2×2 unit matrix and the Pauli matrices, respectively, we find that the anisotropy-induced phases are characterized in terms of $S(S+1) = (\boldsymbol{S}_{2j-1} + \boldsymbol{S}_{2j})^2$ and $S^z = S^z_{2j-1} + S^z_{2j}$ as i) Large-D: $S = 1$, $S^z = 0$; ii) Néel I : $S^z = 0$; iii) Néel II: $S = 1$, $S^z = \pm 1$. Thus, the large-D and Néel II phases appear in a spin-1 chain as well, while the Néel I phase is characteristic of the spin-$\frac{1}{2}$ chain. No ferromagnetic correlation between any neighboring spins in the Néel I phase can be understood by rewriting the Hamiltonian as

$$\mathcal{H} = \frac{1}{2}DN + \sum_{j=1}^{N}\Big[-\frac{J_{\rm F}}{2}(S^+_{2j-1}S^-_{2j} + S^-_{2j-1}S^+_{2j}) + (2D - J_{\rm F})S^z_{2j-1}S^z_{2j} + J_{\rm AF}\boldsymbol{S}_{2j}\cdot\boldsymbol{S}_{2j+1}\Big]. \quad (10)$$

With increasing D, the ferromagnetic coupling is reduced and turned into an antiferromagnetic one.

We have already observed in Fig. 1 that the spin-$\frac{1}{2}$ open chain also exhibits effective moments of $S = \frac{1}{2}$ at each end. In the isotropic case, there appears an alignment of the type $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\cdots$ at a chain end. On the way from the Haldane to Néel II phases, such an alignment remains unchanged and monotonically grows into a long-range order, which is convincing on the analogy of our experience for a spin-1 chain [41]. On the ways to the Néel I and large-D phases, on the other hand, we have novel observations peculiar to the spin-$\frac{1}{2}$ chain. Figure 5 shows the edge moments as functions of D. On both the ways from the Haldane to Néel I and large-D phases, the spin alignment changes with increasing D from $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\cdots$ to $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\cdots$ via $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\cdots$. The ferromagnetic alignment at a chain end is another interesting effect of D and is induced near $D/J_{\rm AF} = 0.22$ and $D/J_{\rm AF} = 0.5$ in the cases of $J_{\rm F}/J_{\rm AF} = 0.5$ and $J_{\rm F}/J_{\rm AF} = 2.0$, respectively. The magnetic moments in z direction form a long-range order in the Néel phases, whereas they vanish in the large-D phase. The total moment induced at a chain end, $\sum_{j=1}^{N/2}(S^z_{2j-1}+S^z_{2j}) \equiv S^z_{\rm edge}$, is variationally expressed as

$$S^z_{\rm edge} = \frac{1}{2}\left[1 - \Big(\frac{|b|^2+|c|^2-2|a|^2}{|b|^2+|c|^2+2|a|^2}\Big)^{N/2}\right]. \quad (11)$$

The absolute value of the fraction $(|b|^2 + |c|^2 - 2|a|^2)/(|b|^2+|c|^2+2|a|^2)$ is smaller than unity in the Haldane phase, while it is fixed to unity in any other phase. Thus, the effective moment of $S = \frac{1}{2}$ persists in the edge of an infinite chain throughout the Haldane phase and disappears with the collapse of the Haldane gap.

Possible dipole-dipole and/or anisotropic exchange interactions between ferromagnetically coupled two spins act as a fictitious single-ion anisotropy [15] and high-frequency electron-spin-resonance experiments on $IPACuCl_3$ [16] indeed revealed the nondegenerate triplet excitation. Therefore, we take more and more interest in nonmagnetic-ion substitution at the Cu site of spin-$\frac{1}{2}$ ferromagnetic-antiferromagnetic bond-alternating chain compounds. The present system may be compared with further polymerized bond-alternating copper(II) complexes such as the trimerized chain compound $3CuCl_2{\cdot}2dx$ (dx = 1,4-dioxane = $C_4H_8O_2$) [42] and the tetramerized chain compound $Cu(3\text{-}Clpy)_2(N_3)_2$ (3-Clpy = 3-chloropyridine = C_5ClH_4N) [43], which behave as a spin-$\frac{3}{2}$ critical antiferromagnet [44, 45] and a spin-$(\frac{3}{2}, \frac{1}{2})$ ferrimagnet [46], respectively. With bond alternation, impurity-induced magnetic effects vary with the location of the dopant impurities in general, as is shown in Fig. 2. A comparative study on the edge states of various bond-alternating chain compounds will lead to brand-new observations.

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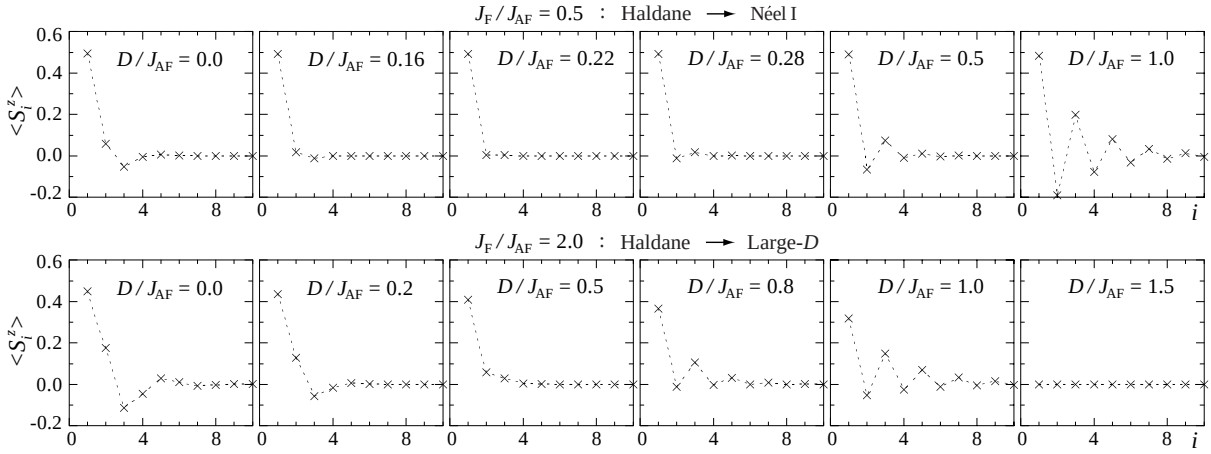

FIG. 5: The matrix-product variational (MP) calculations of the spin moments in z direction for the anisotropic open chains.

[1] F. D. M. Haldane: Phys. Lett. **93A** (1983) 464.
[2] F. D. M. Haldane: Phys. Rev. Lett. **50** (1983) 1153.
[3] K. Hida: Phys. Rev. B **45** (1992) 2207.
[4] K. Hida: Phys. Rev. B **46** (1992) 8268.
[5] M. Yamanaka, Y. Hatsugai and M. Kohmoto: Phys. Rev. B **48** (1993) 9555.
[6] N. Hatano and M. Suzuki: J. Phys. Soc. Jpn. **62** (1993) 847.
[7] K. Okamoto, D. Nishino and Y. Saika: J. Phys. Soc. Jpn. **62** (1993) 2587.
[8] T. Sakai: J. Phys. Soc. Jpn. **64** (1995) 251.
[9] L. P. Battaglia, A. B. Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani: Inorg. Chem. **19** (1980) 125.
[10] S. A. Roberts, D. R. Bloomquist, R. D. Willett and H. W. Dodgen: J. Am. Chem. Soc. **103** (1981) 2603.
[11] H. Manaka, I. Yamada and K. Yamaguchi: J. Phys. Soc. Jpn. **66** (1997) 564.
[12] M. Hagiwara, Y. Narumi, K. Kindo, T. Kobayashi, H. Yamakage, K. Amaya and G. Schumauch: J. Phys. Soc. Jpn. **66** (1997) 1792.
[13] H. Manaka, I. Yamada, Z. Honda, H. A. Katori and K. Katsumata: J. Phys. Soc. Jpn. **67** (1998) 3913.
[14] H. Manaka, I. Yamada, N. V. Mushnikov and T. Goto: J. Phys. Soc. Jpn. **69** (2000) 675.
[15] H. Manaka and I. Yamada: Phys. Rev. B **62** (2000) 14279.
[16] H. Manaka, I. Yamada, M. Hagiwara and M. Tokunaga: Phys. Rev. B **63** (2001) 144428.
[17] H. Manaka, I. Yamada, Y. Miyajima and M. Hagiwara: J. Phys. Soc. Jpn. **72** (2003) 2694.
[18] S. R. White: Phys. Rev. Lett. **69** (1992) 2863.
[19] S. Miyashita and S. Yamamoto: J. Phys. Soc. Jpn. **62** (1993) 1459.
[20] S. Miyashita and S. Yamamoto: Phys. Rev. B **48** (1993) 913.
[21] S. R. White and D. A. Huse: Phys. Rev. B **48** (1993) 3844.
[22] S. Yamamoto and S. Miyashita: Phys. Rev. B **48** (1993) 9528.
[23] S. R. White: Phys. Rev. B **48** (1993) 10345.
[24] M. Kaburagi and T. Tonegawa: J. Phys. Soc. Jpn. **63** (1994) 420.
[25] S. Yamamoto: J. Phys. Soc. Jpn. **63** (1994) 4327.
[26] S. Yamamoto and S. Miyashita: Phys. Rev. B **51** (1995) 3649.
[27] E. S. Sørensen and I. Affleck: Phys. Rev. B **51** (1995) 16115.
[28] T. Tonegawa and M. Kaburagi: J. Phys. Soc. Jpn. **64** (1995) 3956.
[29] S. Yamamoto: J. Phys. Soc. Jpn. **64** (1995) 4051.
[30] S. Yamamoto: Phys. Rev. B **53** (1996) 3364.
[31] I. Affleck, T. Kennedy, E. H. Lieb and H. Tasaki: Phys. Rev. Lett. **59** (1987) 799.
[32] I. Affleck, T. Kennedy, E. H. Lieb and H. Tasaki: Commun. Math. Phys. **115** (1988) 477.
[33] M. Hagiwara, K. Katsumat, I. Affleck, B. I. Halperin and J. P. Renard: Phys. Rev. Lett. **65** (1990) 3181.
[34] M. Aikawa, S. Takagi, M. Ito, K. Takeda and H. Deguchi: J. Phys. Soc. Jpn. **65** (1996) 2786.
[35] T. Asano, Y. Ajiro, M. Mekata, K. Kamishima, K. Koui, T. Goto, M. Furusawa and H. Hori: J. Phys. Soc. Jpn. **66** (1997) 460.
[36] H. Yamazaki and K. Katsumata: Phys. Rev. B **54** (1996) R6831.
[37] K. Totsuka and M. Suzuki: J. Phys.: Condens. Matter **7** (1995) 1639.
[38] S. Brehmer, H.-J. Mikeska and U. Neugebauer: J. Phys.: Condens. Matter **8** (1996) 7161.
[39] T. Kennedy: J. Phys.: Condens. Matter **2** (1990) 5737.
[40] A. K. Kolezhuk, H.-J. Mikeska and S. Yamamoto: Phys. Rev. B **55** (1997) R3336.
[41] S. Yamamoto and S. Miyashita: Phys. Rev. B **50** (1994) 6277.
[42] J. C. Livermore, R. D. Willett, R. M. Gaura and C. P. Landee: Inorg. Chem. **21** (1982) 1403.
[43] A. Escuer, R. Vicente, M. S. E. Fallah, M. A. S. Goher and F. A. Mautner: Inorg. Chem. **37** (1998) 4466.
[44] K. Hida: J. Phys. Soc. Jpn. **63** (1994) 2359.
[45] K. Okamoto: Solid State Commun. **98** (1996) 245.
[46] T. Nakanishi and S. Yamamoto: Phys. Rev. B **65** (2002) 214418.